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6. AUTHOR(S) Daniel. A. Buttry			
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4. Employer Identification Number 836000331		5. Recipient Account Number or Identifying Number 5/33126.34804.5		6. Final Report <input checked="" type="checkbox"/> Yes <input type="checkbox"/> No		7. Basis <input checked="" type="checkbox"/> Cash <input type="checkbox"/> Accrual
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Signature of Authorized Certifying Official 					Date Report Submitted 03/19/96	

OFFICE OF NAVAL RESEARCH

FINAL REPORT

PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS REPORT

for

GRANT #: N00014-90-J-1167

R&T Code: 4133019

Chemistry and Physics in Monolayer Assemblies and Thin Films of Redox Species. Electric
Field Effects, Chemical Reactivity, and Interadsorbate Interactions

Professor Daniel A. Buttry

Department of Chemistry
University of Wyoming
Laramie, WY 82071-3838

June 13, 1996

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Objective, approach and conclusions of the effort

The objective of the effort was to study the influence of the interfacial environment at electrode surfaces on the behavior of molecules present at the surface. The main approach was to use the self-assembly method to immobilize fluorescent probe molecules at the surface and then to spectrally interrogate these probe molecules to learn about their response to electrochemically induced changes in the interfacial environment. This effort resulted in the first direct experimental determination of electric field intensities at electrode surfaces.

Listing of all undergraduate and graduate students and postdoctoral fellows supported

Undergraduate students

None

Graduate students

Greg Ostrom (Ph.D., 1990).

Hugh DeLong (Ph.D., 1990).

Tom Schneider (Ph.D., 1993).

Shauna Hiley (Ph.D., 1993).

Xiaoyan Tang (Ph.D., 1994).

Chien-Ming (Jimmy) Peng (Ph. D., 1995).

John Pope (Ph. D., 1995).

James Walker (Ph.D. expected 1997).

Postdoctoral fellows

Dr. Guoying Chen

Dr. Sandra Kimbrell

Professor Zheng Tan (from Changchun Institute of Applied Chemistry, PRC)

Listing of publications, presentations, patents and reports

Publications (see also publications that are under revision listed as Reports below)

- 1) "Environmental Effects on Redox Potentials of Viologen Groups Embedded in Electroactive Self-Assembled Monolayers", H.C. De Long and D.A. Buttry, *Langmuir*, 8 (1992) 2491-96.
- 2) "Measurement of Electric Fields at Rough Metal Surfaces by Electrochromism of Fluorescent Probe Molecules Embedded in Self-Assembled Monolayers", *J. Am. Chem. Soc.*, 114 (1992) 10085-6.
- 3) "EQCM Studies of Adsorption and Desorption of Self-Assembled Monolayers of Alkyl Thiols on Au", T.W. Schneider and D.A. Buttry, *J. Am. Chem. Soc.*, 115 (1993) 12391-97.
- 4) "Control of Access to Surfaces with Self-Assembling Surfactants Bearing Fluorocarbon Chains", S. Hiley and D.A. Buttry, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 84 (1994) 129-140.
- 5) "A Vibrational Spectroscopic Study of the Structure of Electroactive Self-Assembled Monolayers of Viologen Derivatives", X. Tang and D.A. Buttry, *Langmuir*, 10 (1994) 2235-40.
- 6) "Manipulation of Ionic Transport Processes during Redox Cycling for Polymer/Polymer Complex Films of Poly(styrenesulfonate)/Poly(xylylviologen)", G.S. Ostrom and D.A. Buttry, *J. Phys. Chem.*, 99 (1995) 15236-40.

- 7) "Dimercaptan-Polyaniline Cathodes for Lithium Batteries: Addition of a Polypyrrole Derivative for Rapid Charging", T. Tatsuma, T. Sotomura, T. Sato, D. A. Buttry, and N. Oyama, *J. Electrochem. Soc.* 142 (1995) L182-L184.
- 8) "Formation of Dimerized π -Complexes in Self-Assembled Monolayers Containing Radical Cations of Viologens" X. Tang, T.W. Schneider, J. W. Walker, and D.A. Buttry, *Langmuir*, in press.
- 9) "Kinetics of Mediated Electron Transfer between Viologen Groups in a Self-Assembled Monolayer and Metal Complexes in Solution", T.W. Schneider, S. Hiley, J. W. Walker, and D.A. Buttry, *Langmuir*, in press.

Presentations

- 1) "Measurement of Interfacial Electric Fields at Electrode Surfaces", invited talk at Reilley Award Symposium, Pittsburg Conference, Atlanta, GA, March, 1993.
- 2) "Measurement of Electric Fields at Electrode Surfaces", invited lecture at the Japan Electrochemical Society Spring Meeting, Sendai, Japan, May, 1994.
- 3) "Measurement of Electrostatic Characteristics at Electrode Surfaces", Spring Meeting of the Electrochemical Society, San Francisco, CA, May, 1994.
- 4) "Electron Transfer Cross Reactions between Metal Complexes in Solution and Redox Groups in Self-Assembled Monolayers", invited lecture at the 30th International Conference on Coordination Chemistry, Kyoto, Japan, July 1994.
- 5) "Investigations of Electrostatic Characteristics of the Double Layer Using Fluorescent Probes", Fall Meeting of the American Chemical Society, Washington, D.C., August, 1994.
- 6) "Fundamental Studies of Ion-Exchange in Thin Films of Redox Polymers", keynote lecture at the Spring Meeting of the Polymer Society of Japan, Yokohama, Japan, May 1995.
- 7) "A Vibrational Spectroscopic Study of the Redox Behavior of Mixtures of DMcT and Polyaniline and Its Relevance to High Energy Density Batteries", Spring Meeting of the Polymer Society of Japan, Yokohama, Japan, May 1995.
- 8) "Electrochemical Studies of Electroactive and Non-Electroactive Self-Assembled Monolayers: Factors Affecting Electron Transfer and Adsorbate Interactions", Rocky Mountain Analytical Conference, Denver, July, 1995.
- 9) "Amine Reactions at Carbon Fiber Surfaces: A New Paradigm for Interfacial Adhesion in Carbon Fiber/Epoxy Composite Materials", Fall Meeting of the American Chemical Society, Chicago, August, 1995.
- 10) "Use Of Fluorescent Probe Molecules at the Solid-Liquid Interface", Fall Meeting of the Electrochemical Society, Chicago, October, 1995.

Patents

None

Reports

See publication list above, plus (note these will be published in the coming year).

1. J. M. Pope and D. A. Buttry, "Measurements of the Potential Dependence of Electric Field Magnitudes at an Electrode Using Fluorescent Probes in a Self-Assembled Monolayer", submitted to *J. Am. Chem. Soc.* (under revision).
2. J. M. Pope and D. A. Buttry, "Measurement of Through-Space Dipole-Dipole Coupling from Shifts in Vibrational Band Frequencies for a Stilbazolium Derivative Embedded in a Self-Assembled Monolayer", submitted to *Langmuir* (under revision).

3. J. C. Peng and D. A. Buttry, "Immobilization of Amines at Carbon Fiber Surfaces: Relevance to Interfacial Adhesion in Carbon Fiber/Epoxy Composite Materials", submitted to *Langmuir* (under revision).
4. J. C. Peng and D. A. Buttry, "Bonding of Amines to Carbon Fiber Surfaces to Improve and Control Adhesion: A New Paradigm for Adhesion in Carbon Fiber/Epoxy Composite Materials", submitted to *Carbon* (under revision).

List of transitions

None

Highlights

Publications

- 1) "Measurement of Electric Fields at Rough Metal Surfaces by Electrochromism of Fluorescent Probe Molecules Embedded in Self-Assembled Monolayers", J. Pope, S. Kimbrell, Z. Tan, and D. A. Buttry *J. Am. Chem. Soc.*, 114 (1992) 10085-6.

This publication described the first direct, unambiguous measurements of electric fields at electrode surfaces. It revealed that the details of the interfacial structure in adsorbate layers has a profound influence on interfacial electric fields.

- 2) "Manipulation of Ionic Transport Processes during Redox Cycling for Polymer/Polymer Complex Films of Poly(styrenesulfonate)/Poly(xylylviologen)", G.S. Ostrom and D.A. Buttry, *J. Phys. Chem.*, 99 (1995) 15236-40.

This paper demonstrated that it is possible to use rational chemical approaches to manipulate the transport of ionic species in polymer systems. The finding has relevance in technological areas ranging from solid polymer electrolytes e.g. in fuel cells) to thin-film batteries.

- 3) J. C. Peng and D. A. Buttry, "Bonding of Amines to Carbon Fiber Surfaces to Improve and Control Adhesion: A New Paradigm for Adhesion in Carbon Fiber/Epoxy Composite Materials", submitted to *Carbon* (under revision).

This contribution was the first demonstration of the reactions of amines with vinyl groups at carbon fiber surfaces. It presented a new model for adhesion in carbon fiber/epoxy composite materials.

Awards

- 1) Elected to serve on the Editorial Board of *Langmuir*.
- 2) Received a Senior Research Fellowship from the Japan Society for the Promotion of Science to visit Japan in 1995.

Presentations

- 1) "Electron Transfer Cross Reactions between Metal Complexes in Solution and Redox Groups in Self-Assembled Monolayers", invited lecture at the 30th International Conference on Coordination Chemistry, Kyoto, Japan, July 1994.